Silver catalysts for NO_x storage and reduction using hydrogen

David W. J. McClymont,[a,b] Stan T. Kolaczkowski,[b] Kieran C. Molloy,[c] Serpil Awdry[b]
[a]Doctoral Training Centre, Centre for Sustainable Chemical Technologies, [b]Department of Chemical Engineering, [c]Department of Chemistry, University of Bath, BA2 7AY, UK.
e-mail: D.W.J.McClymont@bath.ac.uk: URL:http://www.bath.ac.uk/csct

Introduction

Legislation is in place to control emissions from various pollutant processes *i.e.* the Waste Incineration Directive (WID) regulates activities that involve burning or gasification of waste (Figure 1)

Technologies have been developed which react a reductant with NO_x emissions, forming harmless N_2 and H_2O. Development of a material and process to treat NO_x emissions using H_2 is the aim of this project

Utilising H_2 already present in the system (Figure 1) could provide a reductant which does not have to be specially manufactured (in contrast to *e.g.* NH_3, urea), and hence would be a cleaner approach

H_2 can also be used in NO_x storage and reduction (NSR) processes where NO_x species are first 'trapped' and subsequently reduced through alternate lean and rich-burn cycles (Figure 2)

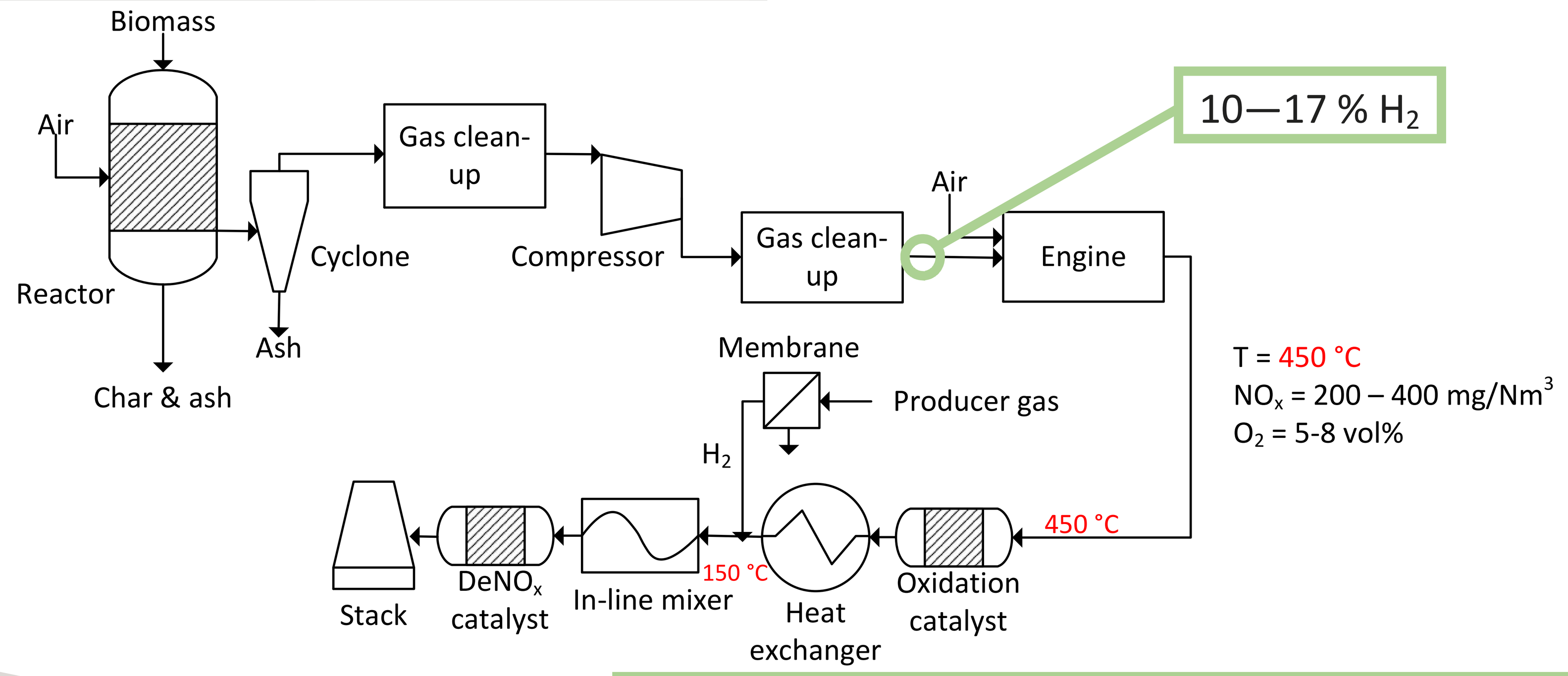

Figure 1: Schematic of proposed biogas engine exhaust treatment system

1. Close proximity of Pt/Ba sites result in the rapid uptake of NO_x at these locations
2. Ba sorbate sites further away from Pt sites have a slower uptake
3. Ba sites not in contact with Pt sites trap NO_2 exclusively from the gas phase using the NO_2 disproportionation mechanism

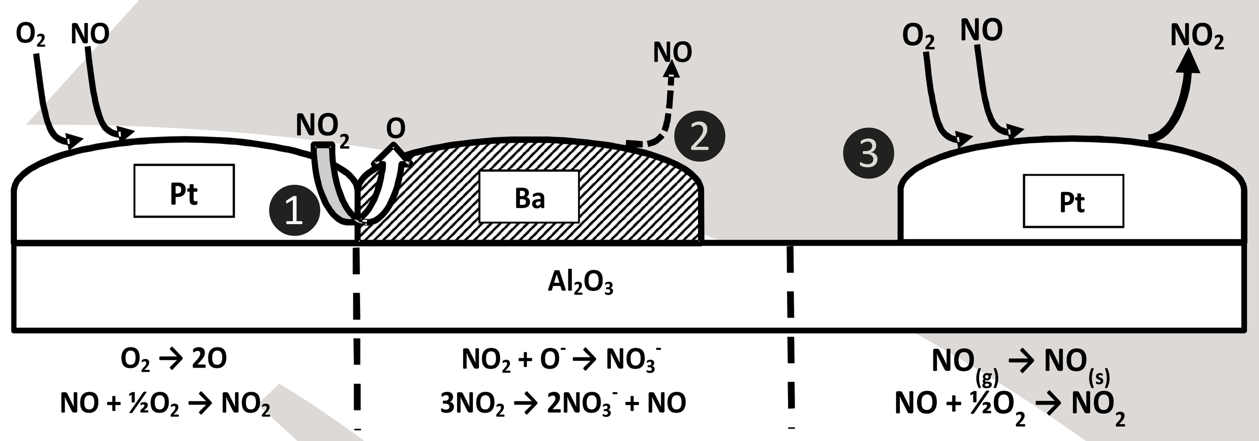

Figure 2: NO adsorption pathways on $Pt/Ba/Al_2O_3$ NSR catalysts

Theory

$Pt/Ba/Al_2O_3$ is considered the 'standard' NSR catalyst and has been extensively studied for this process since original publication by Takahashi *et al.* (1996). As such, the chemical processes involved during NSR cycles are well understood

NSR catalysts generally consist of a noble metal and 'storage component' (alkaline earth metal) supported on alumina. Operating through alternate lean and rich conditions, the NO_x is initially 'stored' on the catalyst surface during lean conditions (Figure 2), in the form of nitrates and nitrites. Subsequent introduction of a reductant, in this case H_2, reduces the stored species to form N_2

Although silver catalysts have previously been explored for related deNO_x applications , primarily in Selective Catalytic Reduction (SCR) approaches (*e.g.* Burch *et al.* (2004), their performance in NSR reactions has not been reported

Catalysts

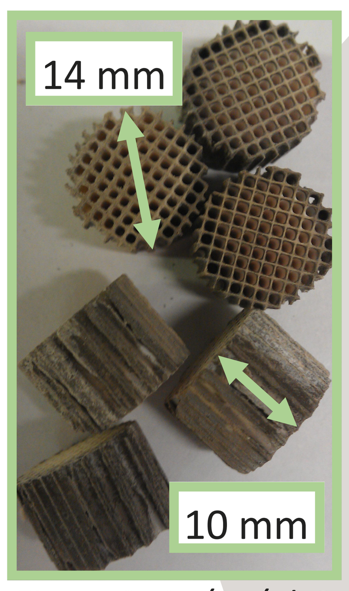

Figure 3: $Ag/Ba/Al_2O_3$ monolith catalysts

Catalysts prepared using impregnation techniques and supported on honeycomb monoliths (Figures 3 & 4)

Table 1: Catalyst Compositions

Loading (wt%)		
Silver	Storage Component	
	Barium	Potassium
5	14	-
5	-	38

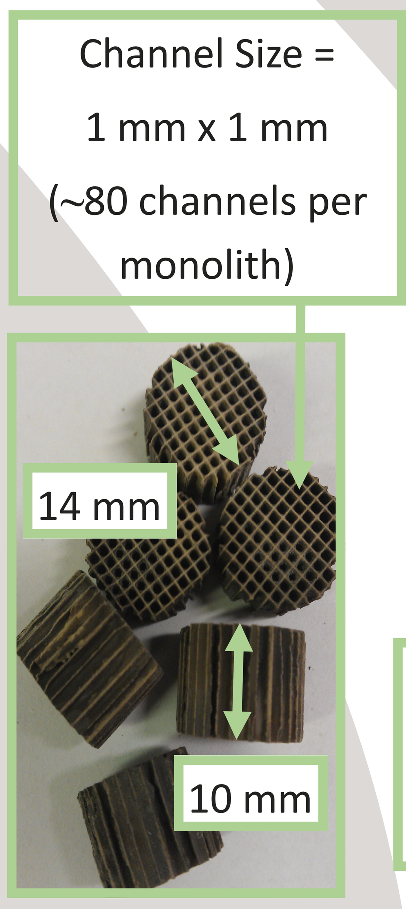

Figure 4: $Ag/K/Al_2O_3$ monolith catalysts

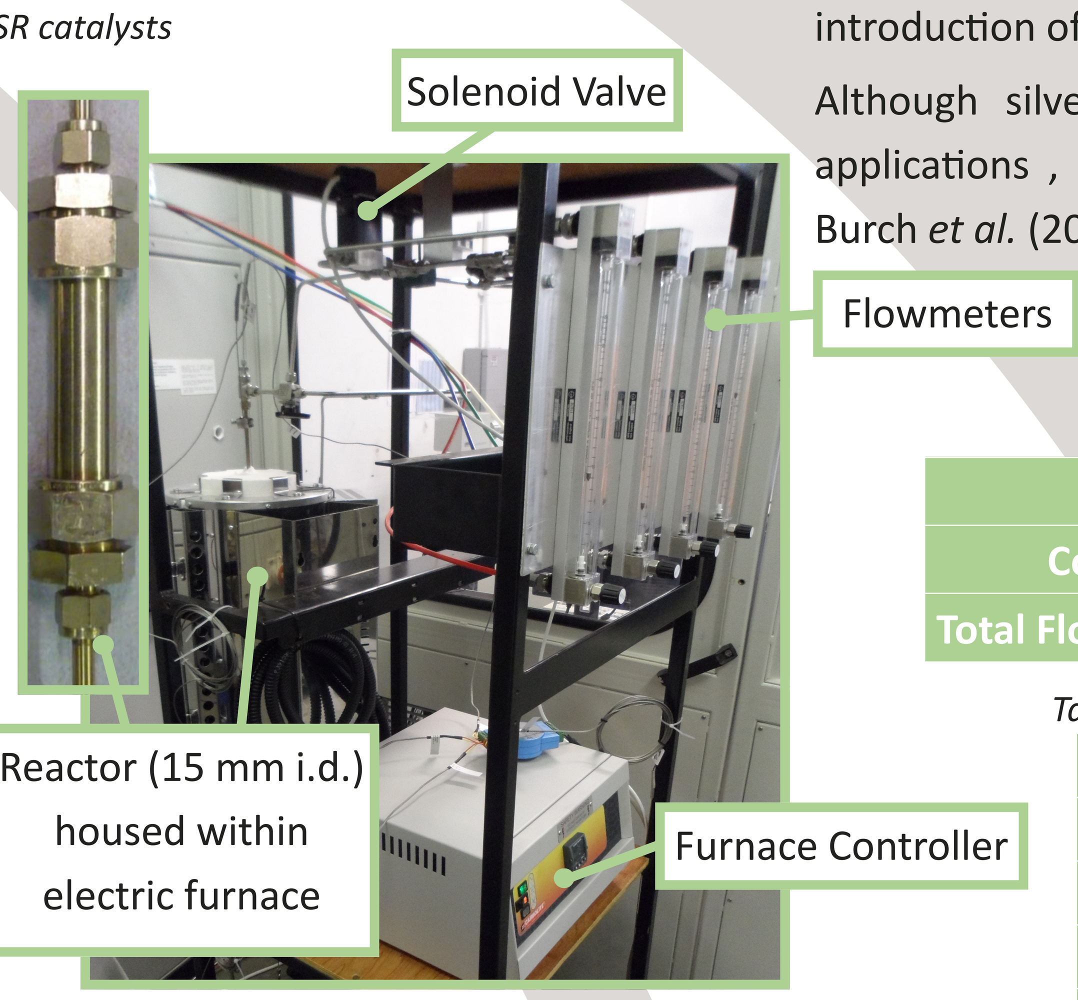

Figure 5: Photo of experimental set-up

Experimental

Table 2: NSR Experimental Conditions

Phase	Lean	Rich
Composition	1000 ppm NO, 3.3 % O_2, N_2	2500 ppm H_2, N_2
Total Flow Rate (ml/min)	480	550

Table 3: Temperature-programmed Desorption (TPD) Experimental Steps

Step 1	Heat to 500 °C under N_2
Step 2	Reduce in 8000 ppm H_2/N_2 for 30 mins
Step 3	Pre-oxidize in 10 % O_2/N_2 for 15 mins
Step 4	Cool down to 150 °C in N_2
Step 5	1000 ppm NO/N_2 for 30 mins
Step 6	Heat to 700 °C in N_2 at 10 °C/min

Results

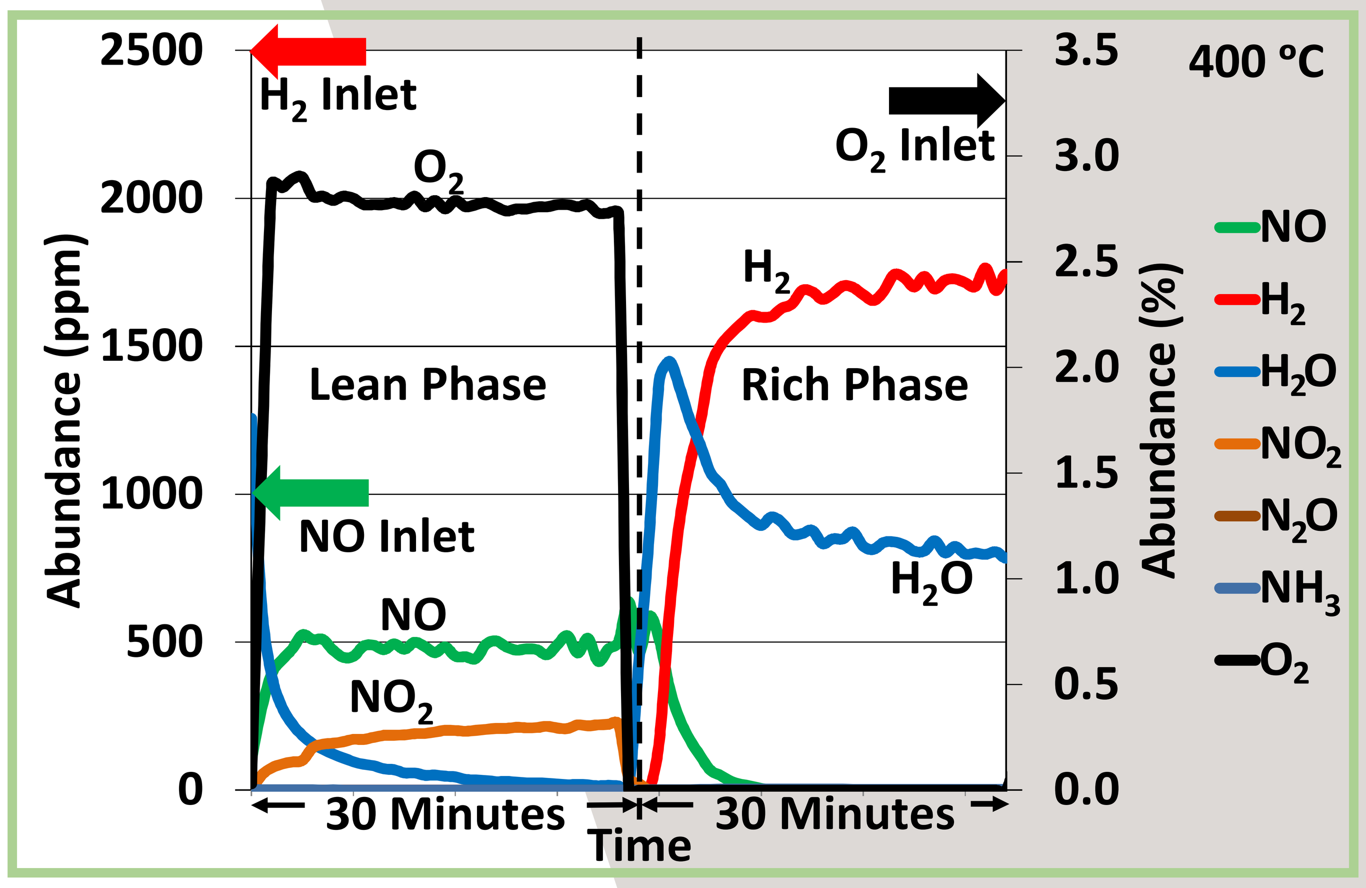

Figure 6: H_2-NSR Lean and Rich cycle over $Ag/Ba/Al_2O_3$ catalyst at 400 °C

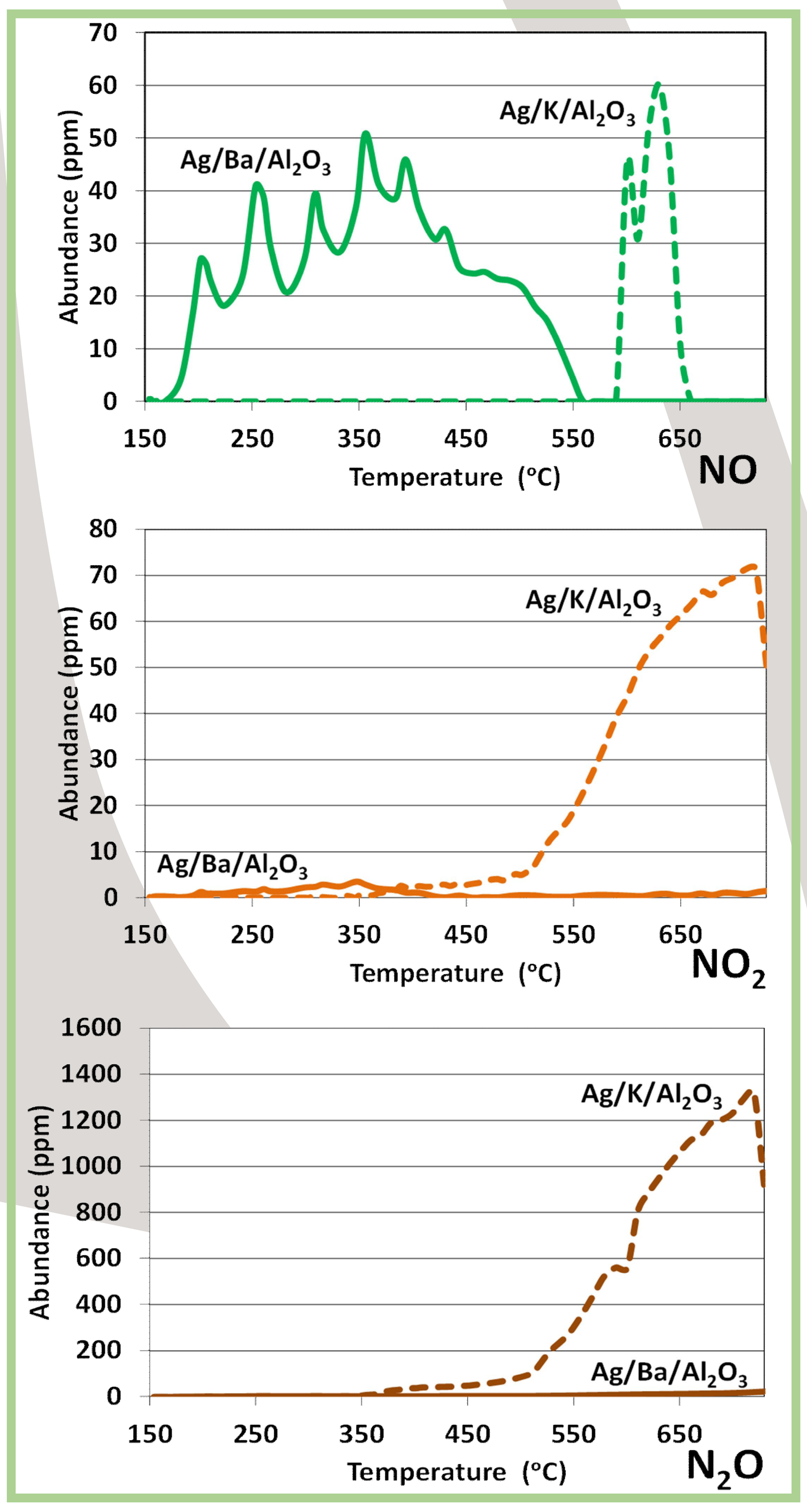

Figure 7: NO-TPD over $Ag/Ba/Al_2O_3$ and $Ag/K/Al_2O_3$ catalysts

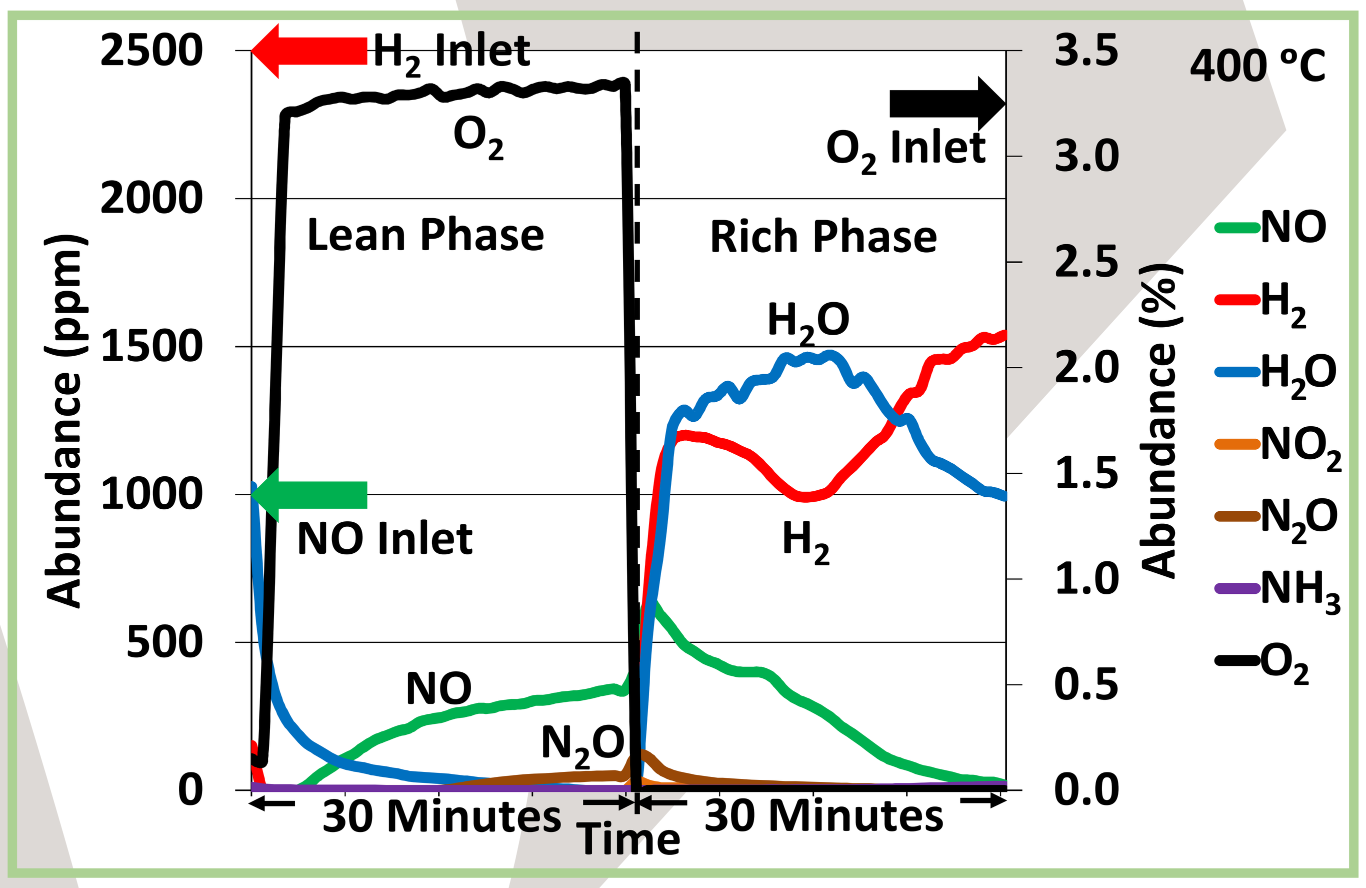

Figure 8: H_2-NSR Lean and Rich cycle over $Ag/K/Al_2O_3$ catalyst at 400 °C

Conclusions

Both catalysts appear to demonstrate some potential in their ability to 'store' and subsequently reduce NO (Figures 6 and 7). Ag/K offers a greater storage capacity (which may be related to storage component loading) and less formation of side products. Ag/Ba demonstrates a greater ability to reduce the stored NO_x with minimal NO desorption seen in the rich phase

Both catalysts demonstrate different affinities for NO (Figure 7), with Ag/K demonstrating reaction of surface species with NO, even in the absence of O_2: formation of N_2O (+1200 ppm) and NO_2 at higher temperatures

Future Work

Complete catalyst characterization including Temperature-programmed Surface Reaction (TPSR) studies

Investigate possible impact of 'KK leaves' Al_2O_3 support structure (Figure 9); freeze drying process produces thin leaves of Al_2O_3 (thickness 0.2-0.8 μm), first reported by Kolaczkowski *et al.* (2006). The thin layer structure may offer less resistance to diffusion, possibly impacting the quantity of catalyst required

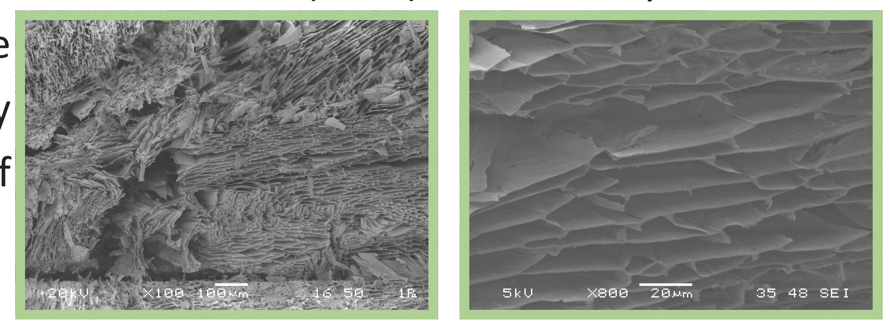

Figure 9: SEM images of Al_2O_3 'KK Leaves'

References

Takahashi, N. et al. (1996). The New Concept 3-Way Catalyst for Automotive Lean-Burn Engine: NO_x Storage and Reduction Catalyst. Catalysis Today, Vol. 27, No. 1-2, pp. 63-69.

Burch, R. et al. (2004). Exceptional Activity for NO_x Reduction at Low Temperatures Using Combinations of Hydrogen and Higher Hydrocarbons on Ag/Al_2O_3 Catalysts. Topics in Catalysis, Vol. 30/31, No. 1-4, pp. 19-25.

Kolaczkowski, S. T. et al. (2006). Novel Alumina `KK Leaf Structures' as Catalyst Supports. Catalysis Today, Vol. 117, No. 4, pp. 554-558.

Centre for Sustainable Chemical Technologies
UNIVERSITY OF BATH
EPSRC
Engineering and Physical Sciences Research Council